## KOKAI PATENT APPLICATION NO. SHO 61-3743

# LAMINATE HAVING A MULTI-COLORED DESIGN

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# LAMINATE HAVING A MULTI-COLORED DESIGN

[Kohsai moyoh o yuhsuru sekisohtai]

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[There are no amendments to this patent.]

### Specification

### 1. Title of invention

Laminate having a multi-colored design

#### 2. Claim of the invention

- (1) A larminate having a multi-colored design in which a transparent metal compound thin film layer (B) having a difference in index of refraction of at least 0.05 with that of molding (A), and a transparent resin layer having a relief pattern on the surface (C) having a difference in index of refraction of at least 0.05 with that of the aforementioned metal compound thin film layer (B) are laminated onto the surface of molding (A) in the order of A/B/C or A/B/C/B.
- (2) The laminate having a multi-colored design described in claim 1 of invention in which the thickness of the aforementioned transparent metal compound thin film layer (B) is in the range of 50-2000 Å and the thickness of the aforementioned transparent resin layer (C) is in the range of 100-10000 Å.
- (3) The laminate having a multi-colored design described in claim 1 of invention in which the aforementioned transparent metal compound thin film layer (B) comprises a laminate

consisting of at least two different substances.

- (4) The laminate having a multi-colored design described in claim 1 of the invention in which the aforementioned molding (A) is a synthetic resin film.
- 3. Detailed description of the invention

[Purpose of invention]

# (1) Field of industrial application

The present invention pertains to novel moldings having multiple colors and mainly used for decoration.

### (2) Prior art

A variety of plastic moldings having a multi-colored design on the surface have been proposed and for example,

- (a) a laminate produced by a method where multiple special compounds such as zinc sulfide, titanium oxide, tin oxide, magnesium fluoride, and copper iodide are deposited,
- (b) a laminate where titanium oxide and a thin film layer are laminated as described in Japanese Kokoku [Examined] Patent Application No. Sho 37-8731,
- (c) a molding having a multi-colored design comprising a light reflective film, an interference resin film with a rugged design and a semi-transparent metal thin film, etc. can be mentioned.

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However, each of the aforementioned laminates and manufacturing methods have disadvantages. For example, in the method described in (a) above, in general, a special lamination layer is required and it is expensive, and in the aforementioned method, it is necessary to deposit the aforementioned material to form a relief pattern on the surface with an optical thickness of at least 1000 Å; thus, it is not suitable for mass production, and adjustment of the multi-colored design produced to a desired pattern is difficult.

Furthermore, in the method described in (b), titanium tetrachloride gas is used; thus, it is accompanied by the formation of hydrochloric acid gas which has an adverse effect on the health of workers, corrosion of equipment, the environment, etc. And furthermore, in the method described in (c), the multi-colored design becomes opaque, thus, the appearance of the molding is lost. In particular, when the molding is transparent, the surface is completely shielded and production of a transparent rainbow molding is not possible.

## (3) Detailed description of the invention

The purpose of the present invention is to improve the aforementioned prior art and to produce a laminate having a multi-colored design without losing the appearance of the molding. [Structure of the invention]

The present invention is a laminate having a multi-colored design in which transparent metal compound thin film layer (B) having a difference in the index of refraction of at least 0.05 with that of molding (A), and a transparent resin layer having a relief pattern on the surface (C) having a difference in the index of refraction of at least 0.05 with that of the aforementioned metal compound thin film layer (B) are laminated onto the surface of molding (A) in the order of A/B/C or A/B/C/B.

The molding (A) of the present invention means a molding having a variety of shapes such as a film, sheet, board and block of synthetic resin, paper, wood, glass, etc.

The aforementioned molding may be either multi-colored or transparent. When multi-colored the layer provided over the molding is transparent, thus, a laminate having a beautiful color enhanced by the appearance of the aforementioned substrate molding can be produced. Furthermore, when transparent, the layer having a multi-colored design laminated on top is a transparent material; thus, a beautiful transparent laminate having a multi-colored design can be produced.

For the aforementioned molding, from the standpoint of ease of application of the multi-colored design onto the surface and productivity, a flexible sheet-like material is desirable.

In particular, a synthetic resin film, for example, a polyester type resin such as polyethylene terephthalate and polybutylene terephthalate, polyolefin type resins such as polyethylene and polypropylene, polyamide type resins such as nylon 6, nylon 66, and nylon 12, cellulose type resins such as polynitrocellulose and polyacetate cellulose, films comprising organic resins such as polyvinyl alcohol, polyethylene tetrafluoride, polycarbonate, polymethyl methacrylate, polyimide, vinyl chloride and vinylidene chloride, etc. can be mentioned as specific examples and either a single layer or two or more laminated layers may be used.

The aforementioned transparent metal compound thin film layer (B) used in the present invention is a metal compound such as titanium oxide, silicon oxide, zinc oxide, antimony oxide, zinc sulfide, cadmium sulfide, magnesium fluoride, cerium fluoride, and cryolite and is a transparent thin film layer having a difference in index of refraction with that of the aforementioned molding (A) of at least 0.05. When the difference in the index of refraction between the aforementioned molding (A) and the aforementioned transparent metal compound thin film layer (B) is less than 0.05, a clear multi-colored design cannot be achieved.

Furthermore, the aforementioned substance used as transparent metal compound thin film layer (B) has a high index of refraction and is transparent and the difference in the index of refraction with the aforementioned molding (A) and the transparent resin layer having a relief pattern on the surface. The substance used for formation of the aforementioned transparent metal compound thin film layer (B) is not especially limited as long as the difference in the index of refraction with the aforementioned molding (A) and the transparent resin layer is at least 0.05 and is capable of forming a transparent thin film layer.

Furthermore, it is not necessary for the aforementioned transparent metal compound thin film layer (B) to be a single material and a laminate of two or more thin film layers made of different materials having a difference in the index of refraction with the aforementioned molding (A) or the transparent resin layer of at least 0.05 may be used.

The aforementioned transparent metal compound thin film layer (B) is laminated onto the

surface of the aforementioned molding (A) using a conventional method, for example, a vacuum deposition process or chemical deposition process such as resistance heating, high-quality heat deposition process, sputtering process, or ion plating process to form the thin film layer.

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The thickness of the aforementioned transparent metal compound thin film layer (B) is in the range of 50-2000 Å and a layer with high transparency is required. When the aforementioned thickness is 50 Å or below or 2000 Å or above, production of the final laminate having a multi-colored design with good appearance is not possible. Furthermore, when the difference in the aforementioned transparent metal compound thin film layer (B) with the aforementioned molding (A) is 0.05 or below, production of the final laminate having a multi-colored design with good appearance is not possible.

Furthermore, the transparent resin layer (C) used in the present invention is a coated film of a single transparent resin or mixture of transparent resins such as multi-colored or colorless transparent acrylic resins, urethane resins, cpoxy resins, nitrocellulose resins, amino alkyd resins, polyester resins and urea-melamine resins. For the aforementioned transparent resin layer (C), the surface with a non-uniform thickness rather than uniformly coated film is required, and a thickness in the range of 100-10000 Å is further desirable. Furthermore, in order to achieve a beautiful a multi-colored design, it is desirable when the difference in the thickness between the recessed member and projected member on the aforementioned layer is in the range of approximately 500-20000 A. When the difference in the thickness is outside the aforementioned range, a multi-colored design cannot be formed and the entire laminate becomes achromatic.

Coating of the aforementioned resin layer (C) can be achieved by a conventional resin coating method and printing method such as roll coating method, spray coating method, dip coating method, spin coating method and gravure coating method.

The aforementioned transparent resin layer (C) is not limited to the aforementioned variety of resins as long as the index of refraction of the resin with the aforementioned transparent metal

compound thin film layer (B) is at least 0.05. When the aforementioned molding (A), transparent metal compound thin film layer (B) and transparent resin layer (C) are laminated in the order of A/B/C, a multi-colored design can be achieved based on the difference in the index of refraction and the relief pattern on the surface of layer (C) and a beautiful a multi-colored design cannot be achieved when the layer structure of A/C/B or B/A/C is used.

Furthermore, when layer B is further laminated onto the aforementioned layer structure of A/B/C to form A/B/C/B, the density of the multi-colored design can be further increased and the multi-colored design is further enhanced.

For protection of the surface of the laminate having a multi-colored design having the aforementioned structure of A/B/C/B, a protective resin layer may be further laminated onto the outer-most layer (B) or lamination order of A/B/C/B/A may be used. In this case, the aforementioned protective resin layer may comprise the same components used in the aforementioned transparent resin layer (C) or different. Furthermore, the two layers on molding (A) may be the same or different.

### [Effect of the invention]

The laminate having a multi-colored design of the present invention is a laminate having a multi-colored design in which transparent metal compound thin film layer (B) having a difference in the index of refraction of at least 0.05 with that of molding (A), and a transparent resin layer having a relief pattern on the surface (C) having a difference in the index of refraction of at least 0.05 with that of the aforementioned metal compound thin film layer (B) are laminated onto the surface of molding (A) in an order of A/B/C or A/B/C/B; thus, the effects described below can be achieved.

(a) A colorful and beautiful laminate having a multi-colored design based on the surface appearance and color of the aforementioned molding (A) and transparent metal compound thin film layer (B) and transparent resin layer (C) can be produced. The laminate having a multi-colored design of the present invention having beautiful appearance can be used for a variety

of purposes such as yarn, packaging materials, wallpaper, posters, labels, clothes, purses, shoes, and belts.

- (b) Upon adjustment of the thickness of the aforementioned transparent resin layer (C), mass production of laminates having the desired multi-colored design is made possible.
- (c) When a transparent material is used for the aforementioned molding (A), a laminate having a multi-colored design can be produced.

The present invention is explained in further detail with working examples below. [Working Example 1]

Vacuum deposition of zinc sulfide (index of refraction 2.35) was performed for one surface of a biaxially drawn polyethylene terephthalate film (index of refraction 1.65) having a thickness of 25 µm and visible light transmittance of 87% in vacuum of 5x10<sup>4</sup> mm Hg using a bell-jar type deposition apparatus. The thickness of the zinc sulfide layer deposited was 300 Å and the visible light transmittance of the laminated film produced was 76%. A methyl ethyl ketone solution of 10 wt% concentration of nitrocellulose (index of refraction 1.51) was coated onto the thin film layer of zinc sulfide on the aforementioned polyethylene terephthalate film laminated with zinc sulfide with a #8 bar coater to form a horizontal non-uniform pattern with invervals of approximately 3 cm and dried in a hot-air circulating oven at 150°C for 30 seconds.

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The laminated polyethylene terephthalate film produced had a beautiful transparent multi-colored design comprising a horizontal pattern with a blue tint. However, when a transparent adhesive tape was applied to the surface of the aforementioned film coated with nitrocellulose, the multi-colored design disappeared. When the aforementioned adhesive tape was removed from the laminate, the initial state was restored. Furthermore, zinc sulfide was deposited onto the nitrocellulose film on one surface of the aforementioned laminate having a multi-colored design using a bell-jar type vacuum deposition apparatus under a vacuum condition of 5x10-4 mm Hg to

form a thickness of 300 Å. The multi-colored design with a horizontal pattern on the laminate polyethylene terephthalate film produced was enhanced further. When a transparent adhesive tape was applied to the deposited surface of the aforementioned film, the aforementioned beautiful multi-colored design remained unchanged.

## [Working Example 2]

Vacuum deposition of zinc sulfide (index of refraction 2.35) was done for both surfaces of a transparent polymethyl-methacrylate cast sheet (index of refraction 1.50) having a thickness of 25 μm and visible light transmittance of 93% one surface at a time to form a thickness on each surface of 450 Å in a vacuum using a bell-jar type deposition apparatus as in the case of Working Example 1. A tolucne solution of 10 wt% concentration of nitrocellulose (index of refraction 1.51) was coated onto one surface of the aforementioned laminated acrylic cast sheet by a roll coater to form a horizontal pattern and dried in a hot-air dryer at 95°C for 10 minutes. Furthermore, nitrocellulose was coated onto the other surface in such a manner that the coating direction was perpendicular to the aforementioned surface and dried. The acrylic cast sheet produced was a transparent decorative board having a vivid lattice-like multi-colored design.

# [Working Example 3]

One 1000 m roll of a biaxially drawing polyethylene terephthalate film having a thickness of 75  $\mu$  and width of 1 mm with a light blue color (index of refraction 1.65) was prepared and set for a vacuum deposition machine and titanium oxide (index of refraction 2.35) was deposited onto one surface of the aforementioned film in vacuum of  $4 \times 10^{-4}$  mm Hg at a rate of 50 m/min to form a deposition thickness of 500 Å.

Furthermore, ethyl acetate solution of 5% epoxy resin was coated onto the deposited side of the aforementioned film using a gravure roll coater to form a non-uniform horizontal pattern and continuous drying was done for 30 seconds at a temperature of 150°C to produce a beautiful film with a multi-colored design comprising a horizontal pattern with a blue tint.

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